

Japanese Kokai Patent Application No. Sho 56[1981]-158333

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METHOD FOR TREATING WASTE PHOTOGRAPHIC DEVELOPING SOLUTION

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[There are no amendments to this patent.]

Claims

1. A method for treating waste photographic developing solution characterized by the fact that a halogen-containing chemical agent that is adjusted for gradual addition is added to the

waste photographic developing solution to prevent problems of slime generated in said waste solution.

2. The method for treating waste photographic developing solution described in Claim 1, characterized by the fact that the halogen-containing chemical agent is a compound that generates hypochlorous acid, hypobromous acid, or hypoiodous acid in water.

3. The method for treating waste photographic developing solution described in Claim 1 or 2, characterized by the fact that the halogen-containing chemical agent is a mixture of dibromodimethyl hydantoin and dichlorodimethyl hydantoin.

#### Detailed explanation of the invention

This invention pertains to a method for treating waste solution which can prevent problems of slime generated in the waste photographic developing solution. More specifically, this invention pertains to a treatment method characterized by the fact that it can prevent problems of slime generated in waste photographic developing solution by adding a halogen-containing chemical agent that is adjusted for gradual addition to the waste solution.

In the photographic steps of development, fixing, water washing, etc., because the waste solution contains a lot of microbes, nutrients, and gelatin, and the water temperature in the water washing step is 20-35°C, microbes may reproduce easily. For example, let's look at the water washing tank. Slime may occur easily in its water discharge tube, etc., and clogging and other problems may occur in the water discharge tube due to slime. However, recently, from the viewpoint of energy conservation, the hot discharged water from the first water washing tank is used as the heat source of the freshly supplied washing water. In this case, the discharged water flows through a heat exchanger followed by disposal. Consequently, problems of slime that used to occur in the conventional discharged water system tend to occur in the heat exchanger portion, too.

Problems of slime lead to a decrease in the efficiency of the heat exchanger. In the extreme scenario, the pipeline portion in the heat exchanger portion is clogged, so that the function cannot be performed at all. As a result, the system has to be disassembled for cleaning on a regular basis. Such disassembling/cleaning leads to a decrease in productivity, and it is a difficult job. Consequently, improvement has to be made.

In order to solve the aforementioned disadvantages due to problems of slime, the present inventors have performed extensive research on using chemical agents to treat it. As a result of this research, it was found that when a halogen-containing chemical agent that is adjusted for gradual addition is added to the waste solution, no slime is formed. As a result, problems of slime can be prevented entirely. In addition, when a heat exchanger is used, there is no decrease in heat efficiency over the long term, and there is no need for disassembling and cleaning. As a

result, the method for treating waste photographic developing solution of this invention was reached.

That is, this invention provides a method for treating waste photographic developing solution characterized by the fact that a halogen-containing chemical agent that is adjusted for gradual addition is added to the waste photographic developing solution to prevent problems of slime generated in said waste solution.

In the following, this invention will be explained.

In this invention, the waste photographic developing solution includes the waste photographic developing waste solution and the waste fixing solution containing gelatin, and discharged water generated in the water washing step.

Halogen-containing chemical agents that can be used in this invention include compounds that generate hypochlorous acid, hypobromous acid, or hypoiodous acid in water. Examples include halogen elements, including chlorine, bromine, and iodine; salts of hypochlorous acid, such as sodium hypochlorite, potassium hypochlorite, etc.; salts of hypobromous acid, such as sodium hypobromite, etc.; alkali metal salts, such as sodium salts and potassium salts, of trichloroisocyanuric acid and dichloroisocyanuric acid; organic compounds that can generate hypochlorous acid in water, such as dichlorodimethyl hydantoin, etc.; alkali metal salts, such as sodium salts and potassium salts, of tribromoisocyanuric acid and dibromoisocyanuric acid; organic compounds that can generate hypobromous acid in water, such as dibromodimethyl hydantoin, etc.; and compounds that can generate hypochlorous acid and hypobromous acid at the same time, such as chlorobromodimethyl hydantoin, etc. The aforementioned compounds may be added either alone or as a mixture to the waste photographic developing solution. In particular, a good effect can be realized when a bromine-containing chemical agent is added to a chlorine-containing chemical agent for use. For example, a mixture of dichlorodimethyl hydantoin and dibromodimethyl hydantoin is preferred. In this case, the effect of the chemical agent can last for a long time. Because of this advantage, problems of slime due to the waste photographic developing solution can be avoided.

Studies on the method for adding these chemical agents indicate that when the chemical agent is quickly added, the amount of the chemical agent consumed per unit time is large, and the cost is high. On the other hand, when the chemical agent is used intermittently, it is impossible to fully prevent generation of slime in the heat exchanger. On the other hand, if the chemical agent is added gradually, the efficiency is high, and the effect of preventing problems of slime can last for a long time.

As a method for adding the chemical agent of this invention, a means that can be adjusted for gradual addition is used. For example, one may use the method in which a bleaching powder with high solubility in water is used to prepare a concentrated aqueous solution, which is then

added dropwise to the pipeline. For a mixture of dichlorodimethyl hydantoin and dibromodimethyl hydantoin with low solubility in water, one may contain the mixture in a stick, tablet or a simple container which is then directly set in the pipeline or in a preparatory tank connected to the pipeline. The initial amount added is determined by trial and error according to the amount of gelatin and the amount of hypo in the waste solution as well as the addition amount of the halogen-containing chemical agent per unit water. That is, the conditions can be [appropriately] selected.

In the following, this invention will be explained in detail with reference to application examples.

#### Application example

3 sticks (30 g in each stick) of a solid 1:1 mixture of dichlorodimethyl hydantoin and dibromodimethyl hydantoin were placed in the front portion of the heat exchanger in a wastewater treatment system for photographic development/fixing/water washing operation equipped with a 25-L PUC-made preparatory tank for the heat exchanger (flow rate of about 60 L/min, operation time 10 h/day, and water temperature 30-33°C). In this state, waste solution treatment was performed for 10 days. In this treatment, about 60 g (corresponding to 2 sticks) were consumed, and slime did not form in the pipeline or heat exchanger. Consequently, a high efficiency was realized for the heat exchanger.

As a control, heat exchange was performed for wastewater under the same conditions but without using the chemical agent. It was found that slime formed in the pipeline and heat exchanger, the heat exchange efficiency decreased significantly, and it was necessary to disassemble and clean the heat exchanger after use.

## TREATMENT OF WASTE PHOTOGRAPHIC DEVELOPER

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### Abstract

**PURPOSE:** To prevent the occurrence of trouble such as the clogging of a drainpipe or inferior heat conduction due to the formation of slime in the presence of microorganisms by charging a halogen-contg. chemical agent so adjusted as to be dissolved little by little into a waste photographic developer.

**CONSTITUTION:** Compounds such as Cl<sub>2</sub> or other element, NaClO or other salt, trichloroisocyanuric acid, dibromodimethylhydantoin and dichlorodimethylhydantoin each generating HClO, HBrO or HIO in water are supplied separately or combinedly to a waste photographic developer so as to be dissolved little by little. For example, bleaching powder with higher solubility is dropped in the form of a thick soln., and dichlorodimethyl- or dibromodimethylhydantoin with lower solubility is held in a container in the form of tablets and directly placed in piping or put into a preliminary tank. Thus, the waste developer is prevented from causing trouble due to slime in the presence of microorganisms.

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⑯ 写真現像液廃液の処理法

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明細書

1. 発明の名称

写真現像液廃液の処理法

2. 特許請求の範囲

- (1) 写真現像液廃液に、微量ずつ滴出するよう調節されたハロゲン系薬剤を投入して、前記廃液に発生するスライム障害を予防する写真現像液廃液の処理法。
- (2) ハロゲン系薬剤が水中で次亜塩素酸、次亜臭素酸または次亜汎塩素を発生する化合物である特許請求の範囲第1項記載の写真現像液廃液の処理法。
- (3) ハロゲン系薬剤がジブ・モジメチルヒダントイインとジクロロジメチルヒダントイインとの混合物である特許請求の範囲第1項又は第2項記載の写真現像液廃液の処理法。

3. 発明の詳細な説明

本発明は写真現像液廃液処理系中に発生するスライム障害を防止する廃液処理方法であり、

さらに詳しくは、写真現像液廃液処理系中に微量ずつ滴出する様に調節されたハロゲン系薬剤を投入することによって廃液系で発生するスライム障害を防止する処理方法に関するものである。

写真の現像、定着、水洗等の工程に於ける廃液には微生物の養分となるゼラチンが多量に含まれていること及び水洗工程の水温が20~35°Cであることに起因して微生物が繁殖し易い。例えば、水洗タンクを始めとして、その排水管などにはスライムが発生し易く、スライムにより排水管のつまりや他の障害が起る。ところで、最近では衛エネルギーの立場から、写真現像液廃液を含む第1水洗タンクからの温度の高い排水を新たに入つて来る水洗水の熱源として使用すべく、この排水を熱交換器を通して加熱する手段がとらわれる様れたり、このため排水管でのスライム障害が熱交換器部分でも発生する傾向にある。

スライム障害は、熱交換器の効率の低下をも

たらし、極端な場合熱交換器内の配管部のつまりからその機能が全く果せなくなるため定期的な分解掃除を命綱なくされている。この分解掃除は経済と生産性の低下を引き起す問題があり、しかもいわゆるきついな仕事でかいため、その改善が待たれていた。

本発明者等は、これらのスライム障害を化学薬剤による処理により解決出来ないものかと種々検討した結果、ハロゲン系薬剤を廃液に微量ずつ溶出する様に調整したものを廃液中に投入することによつてスライムが発生せず、したがつて全くスライム障害を起さず、更に熱交換機を使用する場合には長期にわたり熱効率の低下がなく分解掃除を必要としない写真現像液廃液の処理方法を見い出し本発明に到達した。

即ち、本発明は、写真現像液廃液処理系中に、微量づつ溶出するよう調整されたハロゲン系薬剤を投入することによつて廃液系で発生するスライム障害を防止する写真現像液廃液の処理法である。

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る化合物である。上記に例示した化合物は単独又は混合して写真現像液廃液に供し得る。特に塩素系薬剤に臭素系薬剤を添加して使用する場合が効率的であり、例をばジクロロジメチルヒダントインとジプロモジメチルヒダントインとの混合物を使用する場合が好ましい。この場合、薬剤効果が長期にわたり持続する利点があり写真現像液廃液によるスライム障害を回避できる。

これらの薬剤の投入方法について、種々検討したところ、薬剤が急速に溶出するような方法では単位時間当たりの薬剤消費量が大きくなり経済的でないこと、また薬剤を間欠的に使用する場合には熱交換器内に生ずるスライムを完全に防止できないことが判明し、薬剤を微量づつ溶出させると効率よく長時間にわたりてスライム障害防止効果が持続できることが明かとなつた。

本発明の薬剤投入方法として、微量づつ溶出するよう調整する手段は、例えば水に対する溶解度が高いさらし粉ではその濃厚水溶液を配管内に滴下するような方法が採り得る。また水

本発明を説明する。

本発明の写真現像液廃液と、ゼラチンを含有する廃液である写真現像液及び定着液の廃液、水洗工場の排水を含むものである。

本発明に適用できるハロゲン系薬剤とは、水中で次亜塩素酸、次亜臭素酸または次亜沃素酸を発生する化合物である。具体的には塩素、臭素、沃素のようなハロゲン原素：次亜塩素酸ナトリウム、次亜塩素酸カルシウム等の水素塩酸塩；次亜臭素酸ナトリウム等で代表される次亜臭素酸塩；トリクロロイソシアヌール酸、ジクロロイソシアヌール酸のナトリウム塩又はカリウム塩等のアルカリ塩、ジクロロジメチルヒダントイン等の水中で次亜塩素酸を発生する有機化合物；トリフルオロイソシアヌール酸やジプロモイソシアヌール酸のナトリウム、カリウム等のアルカリ金属塩、ジプロモジメチルヒダントイン等の水中で次亜臭素酸を発生する有機化合物；及びクロロブロモジメチルヒダントインの如き次亜塩素酸と次亜臭素酸を同時に発生す

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に対する溶解度の低いジクロロジメチルヒダントインとジプロモジメチルヒダントインとの混合物のよきな例では、ステックタブレットのようものを簡単な容器に取めて配管内に直接置くか又は配管に接続する予備タンクに設けるよい。最適の投入量は廃液中のゼラチン量、ハニカ量及び単位水量当たりのハロゲン系薬剤の溶出量によつて試行錯誤により設定し、条件を選択できる。

以下実施例により本発明を更に説明する。

#### 実施例

熱交換器 2.5 t PUC 制の予備タンクを設けた写真現像液定着水洗工場の廃水処理系（流量は約 60 t / 時、1 日当たり 10 時間稼働、水温 30 ~ 33 ℃）にジクロロジメチルヒダントインとジプロモジメチルヒダントインとを 1 : 1 の配合比で混合したスティック状の固形化物 1 本 30 g を 3 本、熱交換器の前部に設けた予備タンク中に投げし、10 日間廃液処理を施した。この

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処理操作によって約60タ (2本相当) のスチ  
ンレスが消費されたが配管及び熱交換器にはス  
ライムが全く発生しなかつたので効率よく熱交  
換が実施できた。

同一条件で同様の熱交換器を施す際に、葉部を  
使用しなかつた場合だけ、配管及び熱交換器に  
スライムが発生し、熱交換効率が著しく低下し、  
専用熱交換器の分解掃除が必要となつた。

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